ELECTRODE STUDIES OF STABILITY CONSTANTS OF Cd-RIVER WATER ORGANIC MATTER COMPLEXES

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SUMMARY

A sample of dissolved river water organic acid (largely fulvic acid) was extracted from the Satilla River and purified. Cd-organic acid complexing studies were performed using potentiometric titrations, with and without a background of Cd^{2+}. Acid dissociation values were obtained from the acid-base titration data using the assumption of the similarity of the system to a polyprotic acid, and Cd-organic stability constants were obtained from titrations with a background of Cd in which the free cadmium ion was followed with a Cd electrode. Results indicate that the non-chelating complexing phenomenon can play an important part at low pH and can explain the change in stability constants with pH noted by other experimenters. This study is of value because of the importance of this non-chelation reaction with toxic metals and their binding strengths, and also because of the demonstration of the relatively new use of the Cd electrode for the direct determination of complexing.

Results indicate that at pH 6.3 Cd-organic complexes form in a 1:1 ratio of chelated to non-chelated complexes. At lower pH levels non-chelated complexes become increasingly important, a result which is of direct interest to those concerned about the environmental impact of the mobilization of toxic metals.

CHAPTER I

INTRODUCTION

The importance of humic materials as complexing agents in soils has been studied by numerous experimenters (see Schnitzer et al., 1972a, for a review), and Beck et al. (1974) discussed the possible role of river water organic material in mobilizing complexed metals in natural waters. These organic compounds can effectively increase the solubility of metals and retard precipitation (Rashid et al., 1973), providing a mechanism for the transport and enrichment of the toxic metals. An examination was made of the mechanism and degree of transport of purified river water organic-cadmium complexes to enable a more complete assessment of the possible impact of the mobilization of toxic metals in marine environments.

River water organic acid in a southeastern Georgia stream has been examined in some detail by Martin (1973) where he concludes that it is primarily composed of the humic material, fulvic acid (see below). The major source of this organic matter is the leaching of the drainage basin by rains and the high organic productivity resulting from areas with abundant vegetation (Beck et al., 1974). The resulting organic rich waters will contain the more acidic and soluble fraction of humic materials, fulvic acid.

Fulvic acid is functionally defined as that portion of the soil material extracted by an alkaline solution which is acid soluble, the insoluble fraction being defined as humic acid. Fulvic acids are character-

istically of a lower molecular weight than humic acids (number average molecular weights ranging from 175 to 3570--Schnitzer and Skinner, 1968), and humic acids also vary widely with weights from 1000 to more than 100,000 (van Diyk, 1971). Fulvic acids are higher in total acidity than humic, with values for the former varying from 8.9 to 14.0 meq/g, and for the latter characteristically varying from 4.85 to 8.7 meq/g (Stevenson, 1972a). A detailed study of the nature of fractionated humic acids has been conducted by Rashid et al. (1971), showing the trend of lower molecular weights and higher total acidities for humic acids.

The origin of these organic substances is still subject to study (Felbeck, 1971). The most widely accepted hypothesis involves the microbial degradation products of plant material and the microbial metabolites which, through chemical oxidation and polymerization, become humic substances. According to this scheme, the original structure of the organic molecule has no bearing on the humic material produced, nor does the formation of fulvic acid rely on the previous formation of humic acid. Another major hypothesis involves the direct chemical and microbial degradation of large organic molecules, such as lignin, into the humic substances, the gradual changes from humic acid to fulvic acid, and the ultimate complete decomposition into CO_2, H_2O, and NH_3. According to this hypothesis, the structure of humic material is related to the original structure in the living organism, in many cases lignin, and continued degradation produces the lower molecular weight fulvic acid. It is important to bear in mind that these organic substances are complex heterogeneous molecules which are functionally defined and fit into no well defined organic class.

The structure of these organic molecules is not well known. Chesire et al. (1967) proposed that humic acids consisted of a polycyclic aromatic core to which were attached polysaccharides, phenols, proteins, and metals. Schnitzer (1971) proposed that fulvic acids are made up of a network of phenolic and benzenecarboxylic acids, joined by hydrogen bonds. This open lattice permits the trapping of various organic molecules such as alkanes and fatty acids as well as possibly pesticides and metal ions and oxides. Schnitzer states that this does not exclude interactions between "peripheral" groups and metal ions or hydroxides. Van Dijk (1971) points out that both polycyclic aromatic cores and isolated aromatic rings linked together through aliphatic chains or saturated cyclic or hydroaromatic units have been hypothesized as the humic acid structure, with supportive evidence for both. He states that either may actually exist, the differences arising as a result of the origin of the humic material. The polycyclic aromatic core would be indicative perhaps of "weathering" of carbonized organic material, while the latter is produced through microbial degradation followed by condensation or polymerization.

One of the important features of the humic material is its ability to complex with metals. The importance of this process has been discussed by many authors (good reviews are given by Mortensen, 1963; van Dijk, 1971, and Schnitzer et al., Chapter 11, 1972). This phenomenon is very important in soils (Wright et al., 1963; Wallace, 1963; and Drozdova, 1968) leading to the mobilization, transport, and redeposition of nutrients through the soils, forming enriched layers in the podzolization process. Stevenson (1972a, 1972b) examined the importance of natural organic matter

in the adsorption of herbicides and the chelation of micronutrients, and also concluded that the humic materials are important carriers of toxic metals in soils, sediments, and natural waters.

Reactions with organic acids and clays have been studied by Greenland (1971) who concluded that humic and fulvic acids can be adsorbed onto clay surfaces through a bridging complex with polyvalent metals, as for example with iron and aluminum. Schnitzer et al. (1972b) studied reactions between fulvic acid and Cu-montmorillonite, and demonstrated that the complexing mechanism with metals in the presence of clays favors reactions with carbonyl groups, a reaction not noted with pure aqueous systems. Rashid et al. (1972) examined the complexing mechanism between humic acids and clay minerals in quite some detail, evaluating the effects of pH and ionic strength on adsorption. They found that decreasing pH or increasing NaCl content (to 3.5%) increased the percent organic matter adsorption. Thus, as the organic rich water enters the estuarine environment the tendency would be to decrease adsorption with increasing pH opposed by a generally greater tendency to increase adsorption with the increase in percent of NaCl.

Rashid et al. (1971) studied in some detail the chemical characteristics of various gel chromatography (Sephadex) fractions of humic acids associated with marine sediments, and determined that the major oxygen containing functional groups were located on the smaller molecular weight fractions. An earlier study by Rashid (1971) investigated the role of these purified Sephadex fractions in complexing di- and tri-valent metals, concluding that the smaller and more acidic fractions complexed with metals more readily than the larger, and that these organic acids are important

in the metal complexing phenomenon. This material had been first fractionated with Sephadex gel and then desalted. Ong et al. (1968) examined the transportation mechanism, questioning whether the organo-metallic matrix existed as a true soluble complex or a colloid. They believed the matrix to be a true solution of macro-ions or negative hydrophilic colloids, exhibiting the properties associated with this kind of colloid, such as "salting out." According to the Fouss effect, a polyelectrolyte in water will dissociate, exhibiting mutual repulsion of negative functional groups. Upon addition of a salt, cations will attach themselves to the functional groups, allowing for a coiled configuration due to a lessening of coulombic repulsion. This in turn causes a squeezing out of water molecules, changing the organo-metallic complex from hydrophilic to hydrophobic. A colloidal-like suspension results. Van Dijk (1971) discusses various aspects of the colloidal chemistry of humic materials in some detail.

The complex interactions between organic material and clays, metals, and other organics as noted above indicates the complexity of the reactions involved in natural systems. Many studies have been conducted to determine the mechanisms and stability constants of organic acid-metal complexes (see Schnitzer et al., 1972a, for a review). Purified acid systems were studied in practically all cases. The major methods used are ion exchange, continuous variations, and potentiometric investigations. Schnitzer and Skinner co-authored a series of papers in Soil Science dealing with the evaluation of stability constants of complexes formed between soil organic matter and a number of different metal ions. Their initial study (Schnitzer and Skinner, 1963) utilized potentiometric, conductimetric,

spectrophotometric and infrared spectroscopy study techniques to give a general picture concerning the molar ratio of the complexes. The fourth paper in the series (Schnitzer and Skinner, 1966) examined the carboxyl and hydroxyl groups in the organic matter and their effects on complexing. The authors selectively blocked the functional groups by various methods (acetylation, saponification, and esterification), and then examined the metal retention of the organic matter when complexed with iron, aluminum, and copper. They found that alcoholic hydroxyls played a very small role in metal retention, while the phenolic hydroxyl and acidic carboxyl groups were equally important in complexing. The fifth and seventh papers in the series dealt directly with the evaluation of conditional stability constants of various species. The fifth paper (Schnitzer and Skinner, 1966) evaluated the constants of Cu^{2+}-, Fe^{2+}-, and Zn^{2+}-fulvic acid complexes using the ion exchange method. Their results showed that the numerical value of the constants were in the order Cu > Fe > Zn which was contrary to the Irving-Williams series of divalent metal ion complexation. Their seventh paper (Schnitzer and Skinner, 1967) dealt with the stability constants of Pb^{2+}-, Na^{2+}-, Mn^{2+}-, Ca^{2+}-, Cu^{2+}-, Co^{2+}-, and Mg^{2+}-fulvic acid complexes. The method of study was again by ion-exchange. At pH 3.5 they established an order for the value of the constants of $Cu^{2+} > Fe^{2+} > Ni^{2+} > Pb^{2+} > Co^{2+} > Ca^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$ which changed to $Cu^{2+} > Pb^{2+} > Fe^{2+} > Ni^{2+} > Mn^{2+} > Co^{2+} > Ca^{2+} > Zn^{2+} > Mg^{2+}$ at pH 5.0. Both orders deviated substantially from the Irving-Williams series. Stability constants for metal-fulvic acid complexes are given in Table 1 (Schnitzer et al., 1972a).

Clark and Turner (1969) later argued that the simplified ion -

exchange method proposed by Martell and Calvin (1952) was not applicable, for the graphical analysis was dependent upon the existence of only a mononuclear complex. Schnitzer and Hansen (1970) re-evaluated this method and the method of continuous variation, concluding that both methods were reliable. They stated that between pH 3 and 5 apparently 1:1 molar (and therefore mononuclear) complexes were formed by Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, Ca^{2+}, and Mg^{2+}. At pH 1.7 and 2.35 fulvic acid formed a 1:1 complex with Fe^{3+} and Al^{3+}, respectively. They also concluded that the complexing constant increases with increasing pH (3 to 5) and decreasing ionic strength. Ardakani and Stevenson (1972) reexamined Schubert's ion exchange technique, and developed a graphical solution that circumvents the necessity for assuming a mononuclear complex. Their results cannot differentiate between chelation and non-chelation reactions however, and are obtained for a single pH value.

Gamble (1970, 1972) conducted potentiometric investigations of purified fulvic acid in order to obtain dissociation constants for the acidic groups. From conductometric titrations he determined that two general types of carboxyl groups were present, and using the concentrations of these groups determined the pH dependent dissociation constants for both by assuming that fulvic acids consisted of polyprotic molecules (see Chapter III, Theory).

From an examination of the papers by Beckwith (1959) and Schnitzer and Skinner (1965), Gamble *et al.* (1970) assume that the predominant form of thecomplex with fulvic acid is a salicylic-type chelate (Figure 1a). By further assuming that the more acidic groups correspond to these salicylic-type groups, they obtained Cu^{2+}-fulvic acid stability constants using an

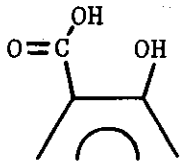
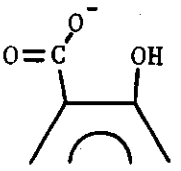
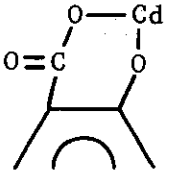
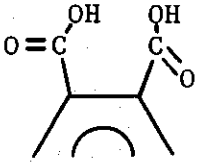
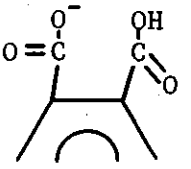
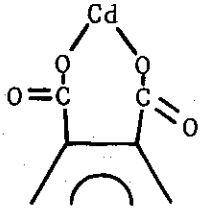
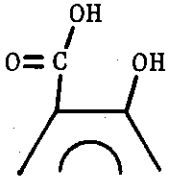
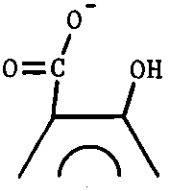
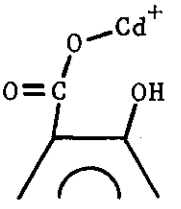
Group	Singly Ionized	Complex
a) Salicylic-chelate			
b) Phthalate-chelate			
c) Salicylic-non-chelate			

Figure 1. Three Possible Types of Metal-Organic Complexing

ion exchange method to determine complexing. Their Job's plot (a plot of mole fraction Cu^{2+} versus molality of bound Cu^{2+}) indicates a 1:1 complexing, which Gamble states as indicating a 1:1 mole ratio of Cu^{2+} to bidendate chelating sites. If non-chelation complexes (Figure 1c) were also to occur with the carboxyl group, the Job's plot would still give the same result. Thus, these complexes should not be ruled out. A phthalate type of chelate (Figure 1b) would move the maximum of the plot to indicate a mole ratio of 1:2, and so phthalate-type chelating does not appear to be significant.

This investigation studied purified river water organic-Cd^{2+} complexes, calculating pertinent stability constants. The Cd^{2+} concentration was followed with an Orion cadmium ion selective electrode, and the possibility of non-chelate cadmium complexes was examined. The purified river water organic is essentially fulvic acid (Martin, 1973), and the results are directly comparable to other metal-fulvic acid stability constants. Work has recently been completed (Cheam, 1973) in which CU(II-)-fulvic acid chelates were examined using an Orion cupric ion selective electrode. The use of these selective ion electrodes will provide a rapid and direct method for determining total complexed metal, enabling a more precise and rigorous examination of the metal-fulvic acid complexing system than previous methods.

CHAPTER II

PROCEDURE

A river water organic acid sample was extracted from a southeast Georgia stream and desalted (see Beck et al., 1974, for the nature of these waters). Some of the purified organic acid was fractionated by Sephadex Gel Chromatography into a higher and a lower molecular weight fraction for a more complete examination of the organic acid and comparison with existing data (Martin, 1973). The purified organic acids were examined by conductometric and potentiometric titrations to determine acidities, and cadmium-river water organic stability constants were obtained for the whole river water fraction from acid-base titrations by following the cadmium background with its ion selective electrode.

Sample Collection and Extraction

In September, 1972, sixty gallons of river water was obtained from County Line Branch, a small stream running between Camden and Brantley Counties. This water contained 132 ppm (ash free) organic matter, determined from the sample volume and weight organic obtained, as compared to an earlier sampling at the same site of 120 ppm organic matter (Martin, 1973). These concentrations are higher than those normally found in river waters of this area (Beck et al., 1974).

The extraction technique was developed earlier with another student in this department (Martin, 1973). The sample, designated RS36-B (Beck

et al., 1974, Figure 1), was at pH 3.8 at collection, and tea-like in appearance. Storage of the sample, and in all subsequent steps except when freeze-dried, was at 4°C under N_2. The extraction procedure began two days after its collection and subsequent storage.

Particulate matter was removed by centrifuging at 12,000 RPM (17,300 G) with a Sorvall Centrifuge, Model SS-3 with rotor type SS-34, equipped with a KSB-3 continuous flow system, flow rate 100-150 ml/min. The sample was concentrated five-fold under vacuum with a Buchler Flash-Evaporator, and the concentrate freeze-dried, yielding 37.5 g.

The organic was redissolved in 1.7 ℓ of distilled water in preparation for desalting. Large insoluble floccules formed, which were removed by centrifugation at 13,000 RPM (20,200 G) at a continuous flow of 25 ml/min. This redissolving procedure is identical to the one used by Martin, when essentially all of his freeze-dried material redissolved. The large floccules which appeared upon resolution might be due to the large amounts of iron present in the system at the collection period, a period of low flushing due to little rainfall. The concentration and freeze-drying process would remove H_2O from the organic molecule, allowing for a theoretical coiled configuration. The trivalent nature of iron and its high stability constant with fulvic acids (Table 1) would cause the formation of very strong complexes, creating a hydrophobic molecule which could be difficult to put back into solution (essentially due to the Fouss effect). One important result of the formation of the floccules is the possibility of an involuntary fractionation, whereby the organic in solution might not be representative of the whole.

Table 1. Log K Values for Fulvic Acid-Metal Complexes, Determined by Ion Exchange (IE) and Continuous Variations (CV) at I = 0.1 (Schnitzer et al., 1972a; p. 221)

	Log K			
	pH 3.0		pH 5.0	
Metal	CV	IE	CV	IE
Cu^{2+}	3.3	3.3	4.0	4.0
Ni^{2+}	3.1	3.2	4.2	4.2
Co^{2+}	2.9	2.8	4.2	4.1
Pb^{2+}	2.6	2.7	4.1	4.0
Ca^{2+}	2.6	2.7	3.4	3.3
Zn^{2+}	2.4	2.2	3.7	3.6
Mn^{2+}	2.1	2.2	3.7	3.7
Mg^{2+}	1.9	1.9	2.2	2.1
Fe^{3+}	6.1[a]	---	---	---
Al^{3+}	3.7[b]	3.7[a]	---	---

[a]Determined at pH 1.70.

[b]Determined at pH 2.35.

Table 2. Partial Analysis of Parent Organic by A.A.S.

Metal	Weight %
Na	< .1
Al	< 0.03
Mg	N.D.
Fe	< 0.1
Ca	< 0.02
K	< 0.01

After the insoluble organic was removed by centrifuging, the solution was desalted by the batch process with AG50W-X8 resin in the H^+ form. Any subsequent desaltings were by this same method. The purified organic was refreeze-dried, and approximately 8 g was obtained. This fraction was denoted the parent fraction, representative of the whole, keeping in mind the possible inadvertent fractionization discussed previously. The organic acid was analyzed for Na, K, Ca, Mg, Al, and Fe by Atomic Absorption Spectrometry (Table 2), and determined to be desalted within the limits of other investigators. Martin (1973), for example, reported an ash content of 2.30% for his RS36A parent fraction, and the metals measured here would account for much less than this.

Organic Fractionation

A 3 g sample of the parent material was fractionated into a higher and a lower molecular weight fraction by Sephadex Gel Chromatography. The chromatographic assembly used for the fractionation procedure was assembled and described previously in some detail (Martin, 1973).

The assembly essentially consisted of a column packed with "Sephadex" G-25 gel, with a controlled volume pump delivering degassed distilled water into the inlet. The column effluent was continuously monitored by a flow-through photometer at 425 nm, and the output recorded on a strip chart recorder. The effluent was collected in 20 ml test tubes with a fraction collector. Three g of the parent fraction was dissolved in 480 ml of distilled water, and injected in 40 ml aliquots into the column via a standardized sample loop between the controlled volume pump and column.

The flow rate was approximately 120 ml/hr, and elution times were on the order of 10 hours. The effluent was separated into an excluded and a retarded fraction on the basis of the recorder absorbance readings (Figure 2), the excluded fraction being eluted first and of an apparent higher molecular weight, the retarded being eluted more slowly. These fractions were subsequently desalted and freeze-dried.

Conductometric Titrations

Conductometric titrations were performed on the parent, excluded, and retarded samples to examine the relative concentrations and types of acidic carboxyl groups (see Gamble, 1970). A Beckman Model RC-18A conductivity bridge and a cell with cell constant 0.1 (as previously measured) were used for all conductivity measurements. Organic solutions were in the range of 0.01 g organic/100 g H_2O, and distilled deionized water was used at all times. Experimentation and storage was under N_2. A stock solution of 0.01N NaOH titrant was prepared with CO_2 free distilled water from a J. T. Baker "Dilut-it", CN4687, and standardized with potassium hydrogen phthalate (KHP).

Organic solutions were prepared by first drying the organic sample at the ambient temperature to a constant weight in a Fisher Thermovac oven over P_2O_5, and then weighing to ± .3 mg. The dried samples were washed into 100 ml volumetric flasks, and made up to mark. The solutions were stirred over a magnetic stirrer, and gently bubbled with prepurified water saturated N_2 to remove CO_2.

Forty ml of the experimental solution were titrated. The titrant was delivered by a 5 ml microburette (reproducible to ± .003 ml) through

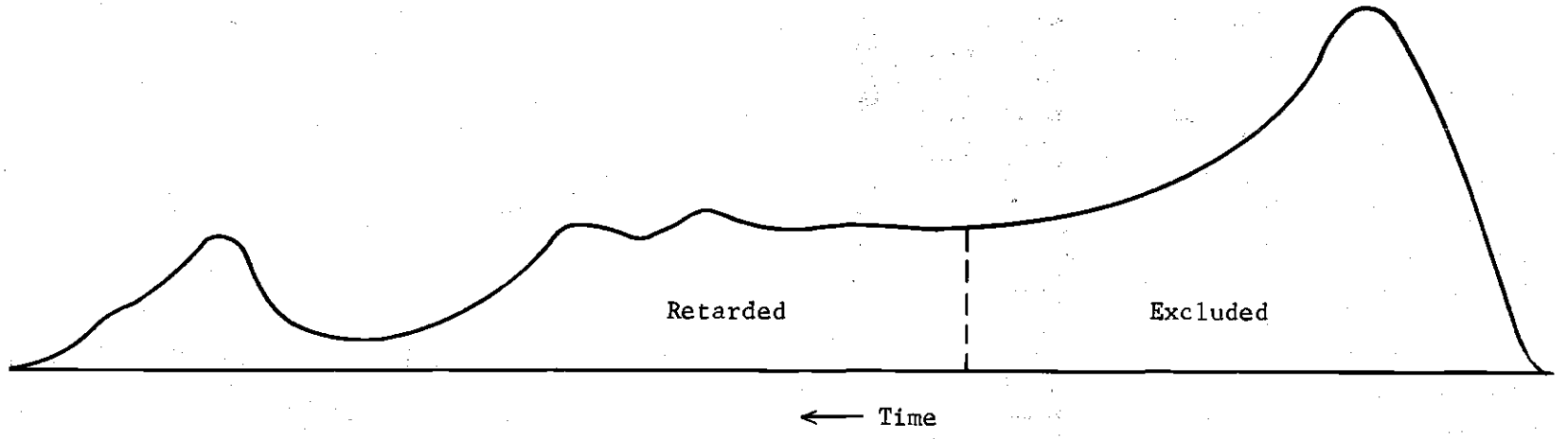


Figure 2. Absorbance Output of Flow-through Photometer at 425 nm. (Areas between dashed marks represent retarded and excluded fractions.)

a rubber stopper which sealed the system. Temperature effects were minimized by placing the experimental system into a 500 ml beaker filled with water at room temperature.

Potentiometric Titrations

Two sets of potentiometric titrations were carried out, the first an acid-base titration requiring only a pH and a reference electrode, now denoted the simple acid-base titration, and another with a background of cadmium using the same system plus a cadmium selective ion electrode, the Cd acid-base titration. pH dependent acid dissociation values were calculated from the simple acid-base titration data according to a generalized method (Fleck, 1966) outlined in Chapter III, Theory. The Cd acid-base titration data and acid dissociation values were used to evaluate stability constants, as also discussed in the section on theory.

All potentiometric titrations were carried out under N_2 at 25.00 ± .05°C in a 250 ml jacketed beaker attached to a constant temperature bath (Figure 3). A pH electrode, Sargent Welch model S-30050-15, and single junction reference electrode, Orion Model 90-01, filled with Orion filling solution 90-00-01, was used for all experiments. pH values were recorded from an Orion Model 801 digital pH meter. The experimental system was sealed with a plexiglass lid through which were inserted the electrodes, a 0-50°C thermometer, and N_2 and titrant delivery tubes. The NaOH titrant was delivered by a 5 ml microburette to which were attached Malcasorb CO_2 absorbers, and the system was stirred over a magnetic stirrer.

The 0.1 N NaOH titrant was prepared from a J. T. Baker Dilut-it, and standardized with KHP. pH standards from 3 to 10 were prepared from

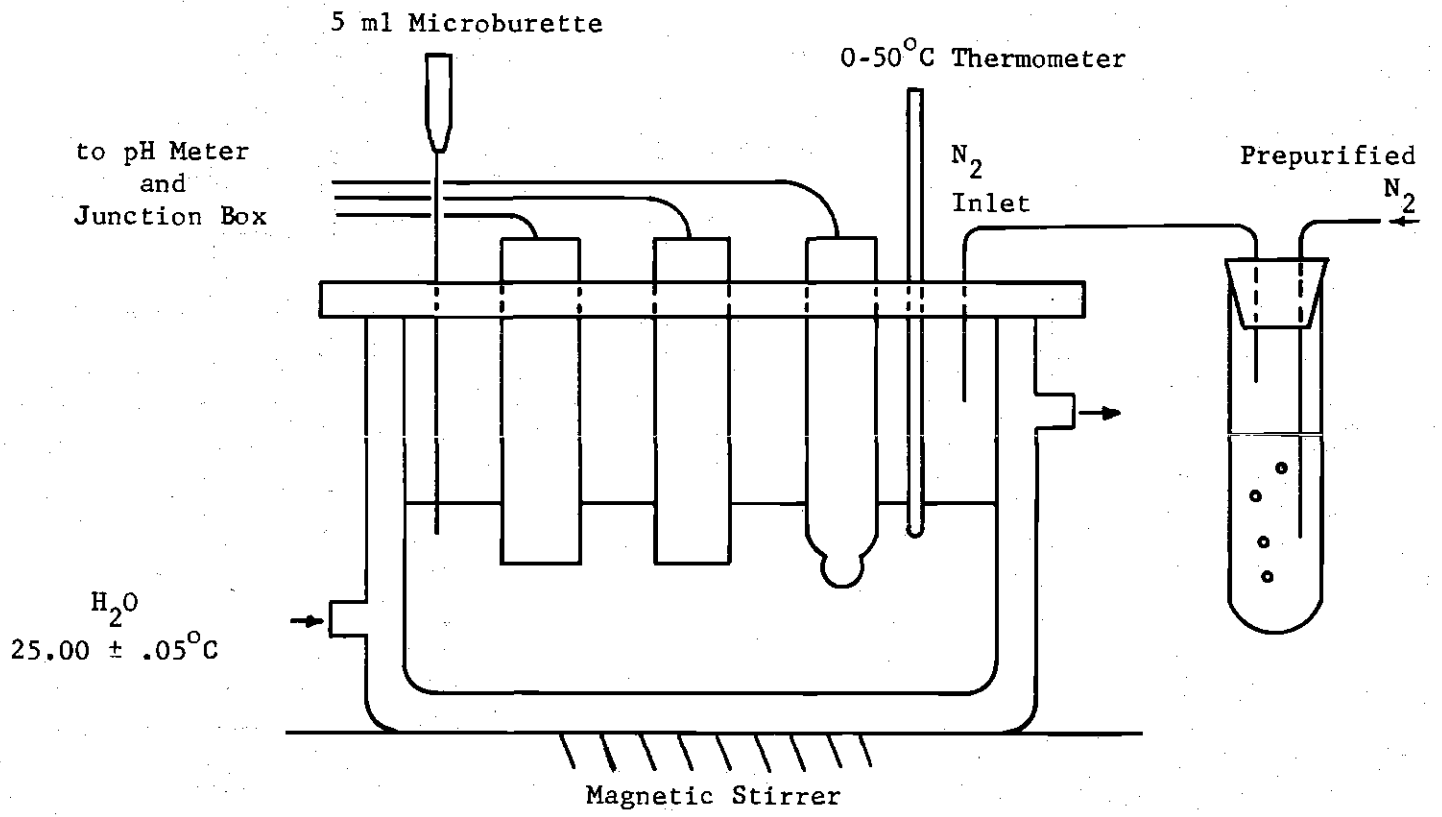


Figure 3. Experimental Apparatus for Potentiometric Titrations (The electrodes are a pH, Cd-Ion, and reference. CO_2 absorbers were attached to the 5 ml microburette.)

Coleman certified buffer tablets. The $Cd(NO_3)_2$, $NaNO_3$, and NaCl used in subsequent titrations were reagent grade.

Simple Acid-Base Titrations

Titrations of the parent organic and excluded and retarded fractions and salicylic acid were conducted in 0.1 N NaCl to maintain a constant ionic strength. The solutions were prepared by drying and weighing approximately 0.1 g organic acid, and adding 150 g 0.1 N NaCl. Actual experimental conditions are contained in Figure 5. In these and all other potentiometric titrations the solutions were allowed to equilibrate at 25.00 ± .05°C in the jacketed beaker while bubbling pre-purified water saturated N_2 through the solution to remove CO_2. During the actual titration the N_2 delivery tube was removed from the solution and a N_2 atmosphere was maintained. Readings were taken while stirring of pH, temperature, and ml after each addition of base, which ranged from 0.3 to 0.05 ml. An additional titration was performed on the parent sample at the same concentration as the Cd acid-base titration using 0.1 N $NaNO_3$ as an ionic strength background. The data from this titration were used for determining the pH dependent acid dissociation values, and the $NaNO_3$ was used so that this titration and the Cd acid-base titration could be directly comparable. The problems of Cd complexing with NO_3^- are much less than with Cl^- (see Appendix). Approximately 100 ml of 0.1 g organic/100 g 0.1 N $NaNO_3$ solution was prepared gravimetrically, and 75 ml was pipetted into the jacketed beaker and titrated.

Cd Acid-base Titration

Only the parent organic acid and salicylic acid were titrated in this manner. Approximately 100 ml of 0.1 g acid/100 g 0.1 M $NaNO_3$ -

10^{-3} M Cd^{2+} solution was prepared gravimetrically, and 75 ml were titrated. The Cd^{2+} stock solution was prepared from $Cd(NO_3)_2 \cdot 4H_2O$ and standardized with Na_2H_2EDTA (Schwartzenbach et al., 1969, p. 264). The Cd electrode was standardized before and after each titration with 10^{-1} through 10^{-5} M Cd^{2+} solutions. The equipment is identical to that outlined already with the following exceptions: an Orion Model 605 Electrode switch enabled the simultaneous use of the pH and cadmium electrodes with the single junction reference electrode and the Orion pH meter. A Beckman 10" recorder with a 0-30 mv variable potentiometer in series with the pH meter was also used to observe the stability of the cadmium readings. The variable potentiometer allowed the use of the highest scale expansion on the recorder to detect small variations in output. The cadmium electrode was an Orion Model 94-48A, and was also inserted through the plexiglass lid. According to the manufacturers specifications, the Cd electrode is pH independent between pH 2 and 8 at the cadmium levels of this experiment, but values below pH 4 were not used because of pH effects noted in this lab. The recommended reference electrode is the Orion Single Junction. The titration proceeded as has already been described, with the exception that mv readings corresponding to Cd^{2+} in solution were also recorded. The titrant was again 0.1 M NaOH.

CHAPTER III

THEORY

The simple acid-base titration data of the parent organic with a $NaNO_3$ background were used to determine pk values for the organic acid. These values were then used in conjunction with the Cd acid-base titration data to examine the types and stability constants of the complexed species.

Activity-Concentration Considerations

By definition thermodynamic stability constants describe the equilibrium conditions of the species of a particular reaction at a given temperature and pressure, where all species are expressed in terms of activities. In many cases this constant is obtained by performing experiments at different ionic strengths and obtaining conditional stability constants, i.e., concentration dependent constants, and then extrapolating back to a zero ionic strength, where activity coefficients approach one and activities and concentrations are identical. The use of selective ion electrodes, which by definition respond to activities of free ions, will enable a more detailed examination of thermodynamic stability constants. While the ultimate goal is to attain these thermodynamic constants, this is a difficult task due to the present absence of information concerning the nature of the species involved and the effects of ionic strength on the organic ions.

In this study only mixed constants were determined whereby all

species are described in terms of concentrations, C, with the exception of H^+. Hydrogen ion values approximate activities, α, being taken directly from pH measurements. Cadmium electrode values also approximate activities but will be converted to concentrations by the simple relationship:

$$(Cd^{2+}) = \frac{[Cd^{2+}]}{\gamma^{+}_{Cd^{2+}}}$$

Throughout this paper parentheses will denote concentration and the brackets activity. The activity coefficient term, γ^{+}_{Cd}, is obtained from Kielland (1937), taken from the Orion cadmium electrode instruction manual. All other activity coefficients are assumed to be constant because of the high ionic strength of the background salt (10^{-1} eq/ℓ). Thus, by definition

$$K^t = \frac{\alpha_A \alpha_B}{\alpha_C \alpha_D} = \frac{C_A C_B}{C_C C_D} \cdot \frac{\gamma_A \gamma_B}{\gamma_C \gamma_D} = K^c \cdot G$$

where G is the activity coefficient term, a constant at constant ionic strength, K^t the thermodynamic stability constant, and K^c the conditional. The conditional constant then is

$$K^c = K^t \cdot \frac{1}{G}$$

In this paper, since pH measurements were used as a measure of H^+, mixed constants will be obtained of the nature

$$K^t = \frac{C_A \alpha_{H^+}}{C_C C_D} \cdot \frac{\gamma_A}{\gamma_C \gamma_D} = K^m \cdot G'$$

The identifying superscripts will not be used and all constants will be either mixed or concentration, depending upon the presence of an $[H^+]$ term in the equation.

pK Values for Polyprotic Acids

The theory and equations presented here are largely from the works of Tanford (1961) and Fleck (1966), concerning the general theory of multiple equilibria. Fulvic acids have been assumed to be polyprotic acids because of their large size and acidities (Gamble, 1970; van Dijk, 1971). These polyprotic acids contain a large number of functional groups, and dissociation constants can be obtained which will be an average constant for the dissociation of the groups at a particular pH. The proximity of the groups also requires the consideration of the effects of an adjoining ionized group which, through charge considerations, will effect the dissociation of neighboring groups. For these reasons, pK values must be obtained throughout the range of the titration. Gamble (1970) obtained pK values for two types of carboxyl groups which he termed Type I and Type II. His Type I groups were the more acidic carboxyls as detected in conductometric titrations, probably salicylic- and phthalate-type carboxyls (Figure 1a and 1b, respectively) while the Type II groups were the less acidic carboxyls.

Because of the absence of a second inflection point in the simple acid-base titrations and the absence of information to adequately describe

the more acidic groups, the titration curve will be assumed to be descriptive of a polyprotic acid consisting of carboxyl groups which are not necessarily chemically identical but whose acid strengths are so similar that no discrete inflection points are observed. The smooth titration curve warrants such an assumption. The resulting pK values will be used to determine the concentration of dissociated groups in solution at a particular pH, enabling a more detailed examination of the complexing process.

In order to express the concentration of these acids in moles per liter, the molecular weight must be known. To circumvent the problems associated with evaluating an average molecular weight for this heterogeneous mixture of organic molecules, all calculations were performed in equivalents of acidic carboxyl per gram of organic acid. The total number of groups per gram was determined directly from the inflection point of the simple acid-base titration curve. A knowledge of the amount of organic in solution enables the expression of the concentration in equivalents of carboxyl groups per liter.

For an acid-base mixture containing known total amounts of a polyprotic acid, C_A, and monovalent base NaOH, C_B, the following conservation equations exist:

$$C_A = \sum_{i=0}^{n} (H_i L^{-(n-i)}) \qquad (1)$$

$$C_B = (Na^+) \qquad (2)$$

where n is the number of functional groups per gram of polyprotic (fulvic)

acid and (Na^+) is the concentration of strong base, NaOH. The corresponding electroneutrality equation is:

$$(OH^-) + \sum_{i=0}^{n} i(H_{n-i}L^{-i}) = (H^+) + (Na^+) \qquad (3)$$

The quantity $\bar{v}$ will be defined as:

$$\bar{v} \equiv \frac{\text{number of protons bound to sites on X grams of acid}}{\text{number of grams of X}} \qquad (4)$$

This can be rewritten as:

$$\bar{v} \equiv n - \frac{\text{number of empty binding sites on X grams of acid}}{\text{number of grams of X}} \qquad (5)$$

Dividing the numerator and denominator of the right hand term in Equation (5) by the solution volume, the fraction can be expressed in terms of concentration, or eq/ℓ. An estimate of $\bar{v}$ can then be made from Equations (1), (2), (3), and (5):

$$\bar{v} = n - \frac{\sum_{i=0}^{n} i(H_{n-i}L^{-i})}{C_A} \qquad (6)$$

$$\bar{v} = n - \frac{(H^+) + (Na^+) - (OH^-)}{C_A} \qquad (7)$$

$$\bar{v} = n - \frac{(H^+) - \frac{Kw'}{(H^+)} + C_B}{C_A} \qquad (8)$$

$\bar{v}$ is evaluated at every point along the titration curve.

To obtain a pK as a function of $\bar{v}$, the acid is assumed to dissociate according to the following scheme:

$$HL = H^+ + L^- \tag{9}$$

$$K(\bar{v}) = \frac{[H^+](L^-)}{(HL^-)} \tag{10}$$

where $K(\bar{v})$ is a general constant descriptive of the overall system, and as such is an average dissociation constant. This term is essentially a weighted average of the discrete dissociation values (Gamble, 1970). Equation (10) can be rewritten as

$$\log K(\bar{v}) = \log [H^+] + \log \frac{(L^-)}{(HL)} \tag{11}$$

$$pK(\bar{v}) = pH - \log \frac{(L^-)}{(HL)} \tag{12}$$

If V is the volume of solution and X the grams of organic acid added,

$$\bar{v} = n - (L^-) \cdot \frac{V}{X} \tag{13}$$

and

$$n = \left((L^-) + (HL) \right) \cdot \frac{V}{X} \tag{14}$$

Equation (12) can be rewritten as

$$pK(\bar{v}) = pH - \log\left(\frac{n - \bar{v}}{\bar{v}}\right) \qquad (15)$$

A value of $pK(\bar{v})$ can be obtained from the values of $\bar{v}$, n, and pH (see the Appendix for sample calculations). Thus, a term can be obtained to describe the degree of dissociation of the carboxyl groups at a particular pH. This chemical picture, while simplified, will enable a more complete description of the complexing process. An important point to remember is that the acid is considered to be theoretically pure, while in fact an examination of the purity of the organic sample (Table 2) revealed the presence of some metals. Due to the absence of information regarding the nature of these cations in the system and since the total carboxyl acidity is inferred from the titration data and should be a measure of the titratable carboxyls in this system, it will be assumed that the $pK(\bar{v})$ values represent a good estimate of the degree of dissociation.

River Water Organic-Cadmium Complexing Constants

In agreement with the generalized equation of Schnitzer *et al.* (1972a) and the results of Gamble (1970), Ardakani *et al.* (1972), and Cheam (1973), the overall complexing reaction will be assumed to be of the form:

$$Cd + L = CdL \qquad (16)$$

$$K_1 = \frac{(CdL)}{(Cd)(L)} \qquad (17)$$

where charges have been ignored and L is the complexing site with carboxyl dissociated (Equation 9). This is analogous to the following equations:

$$Cd + HL = CdL + H^{+} \tag{18}$$

$$K_2 = \frac{(CdL)[H^{+}]}{(Cd)(HL)} \tag{19}$$

$$HL = H^{+} + L \tag{20}$$

$$K_d = \frac{[H^{+}](L)}{(HL)} = K(\bar{v}) \tag{21}$$

where K_d is the dissociation constant already determined, $K(\bar{v})$. Thus, by substitution and rearrangement of (17), (19), and (21),

$$K_1 = K_2/K(\bar{v}) \tag{22}$$

The ligand is assumed to be the dissociated carboxyl group, and the resulting stability constant will be a general term which does not differentiate between non-chelation (Figure 1c) or chelation (Figure 1a) complexes. In the same way, the above investigators assumed or found a 1:1 relationship between metal and bound carboxyl.

The value K_1 is determined as follows: the mass balance equation for total cadmium is

$$C_M = (Cd^{2+}) + (CdL) + (CdX) \tag{23}$$

where C_M is the total cadmium concentration, (CdL) the concentration of complexed metal, and CdX denotes the NO_3^- and OH^- complexes, which are insignificant over the pH range of this experiment (see the Appendix). The corresponding mass balance equation for total organic concentration is

$$C_A = (HL) + (L) + (CdL) \tag{24}$$

where C_A is the total acid concentration, and (HL) and (L) the undissociated and dissociated acid species respectively. Charges are ignored, since again there is no way to differentiate between a chelate or non-chelate type complex. It is assumed that phthalate-type chelates are insignificant, following Gamble (1970) and Schnitzer et al. (1963). This assumption is strengthened in the Job's plot given by Gamble (1970, Figure 1) where he shows that a 1:1 mole ratio of Cu^{2+} to bidentate chelating sites is indicated. Thus, the general expression of (16) and the mass balance equation of (23) are correct descriptions.

By combining and rearranging (21), (23), and (24),

$$(L) = \frac{K(\bar{\nu})\left(C_A - (CdL)\right)}{K(\bar{\nu}) + [H^+]} \tag{25}$$

Since C_M is known and (Cd^{2+}) is directly determined from the Cd electrode measurements, (CdL) can be determined from (23), and (L) can be evaluated from (25). Every term in (17) can be determined, and values of K_1 can be calculated for each pH in the titration (see the Appendix).

This method circumvents the problems of the ion-exchange method

shown by Schnitzer et al. (1972a), where their plot of (L) vs $\frac{\lambda_o}{\lambda} - 1$ apparently uses C_A values rather than (L). It also does not rely on the assumptions that all complexing is a salicylic-type chelate, and that all of the most acidic groups detected by conductometric titrations are these salicylic-type groups (Gamble et al., 1970; Cheam, 1973).

CHAPTER IV

RESULTS

Conductometric Titrations

The results of the conductometric titrations performed on the parent organic and retarded and excluded fractions, as well as on salicylic acid, are given in Table 3 and the titration curves in Figure 4.

Table 3. Conductometric Titration Results (meq/g)

Sample	Minimum	Inflection[a]	Other
Parent	3.97	5.98	6.17[b]
Excluded	3.17	5.36	
Retarded	3.89	6.32	
Salicylic Acid	7.05	--	7.20[c]

[a] Approximate values only, as outlined in text.
[b] From Martin (1973).
[c] Theoretical value.

In agreement with Gamble (1970), the minimum is assumed to correspond to the most acidic groups, probably salicylic and phthalate type, and the inflection to total carboxyl. Because of the similarities in pK values for the first hydrogen dissociation of the two acids (pK_1 = 2.93 for salicylic acid, pK_1 = 2.89 for phthalic acid--Chemical Rubber Company, 1971), little can be said about the exact nature of these groups.

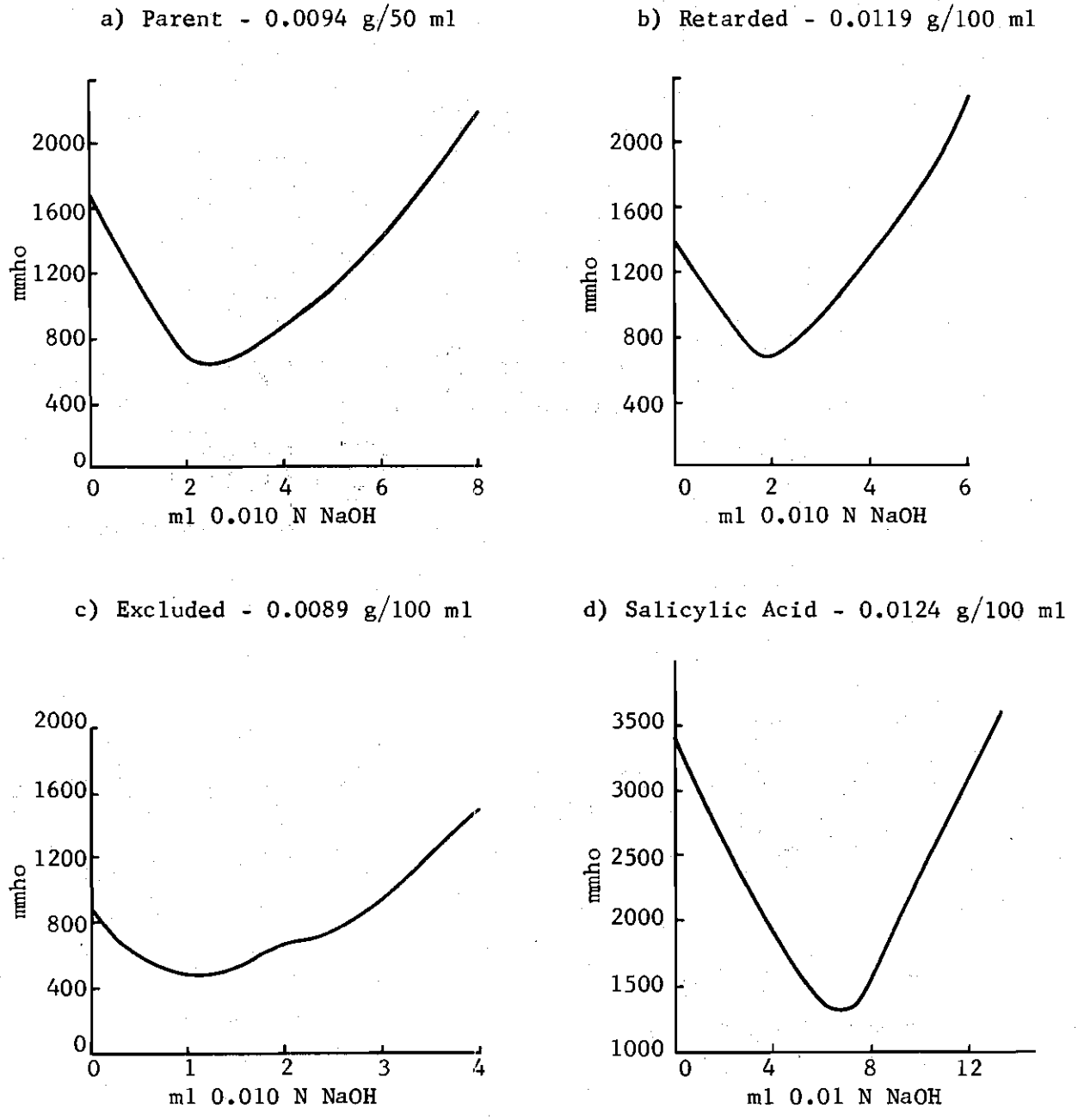


Figure 4. Conductometric Titration Curves (T = ambient temperature, background I = 0, 40 ml titrated)

These results indicate that the smaller molecular weight fraction, the retarded, contains a higher concentration of the more acidic carboxyls than the excluded. The values for total carboxyl are in general agreement with Martin (1973), but should be used with caution due to the difficulty in obtaining an accurate value of the inflection point. A Grans plot (Gran, 1952) failed to reveal a discrete endpoint, and Gamble (1970) also could not detect a discrete endpoint at these concentrations. These values are not important except as indicators of total carboxyl, as the potentiometric titrations reveal the total carboxyl content more precisely. The salicylic acid results indicate an experimental total carboxyl content very similar to the theoretical, and the titration curve does not reveal an inflection due to the phenolic H^+ dissociation.

Potentiometric Titrations

Simple Acid-Base Titrations

The titration curves and experimental conditions of the river water organic acid parent and fractions and of the salicylic acid sample are contained in Figure 5 and inflection point values are in Table 4.

Table 4. Simple Acid-Base Titration Results (meq/g)

Sample	Inflection Point
Parent	6.00
Excluded	5.52
Retarded	5.47
Salicylic Acid	7.05[a]

[a]Theoretical value of 7.20.

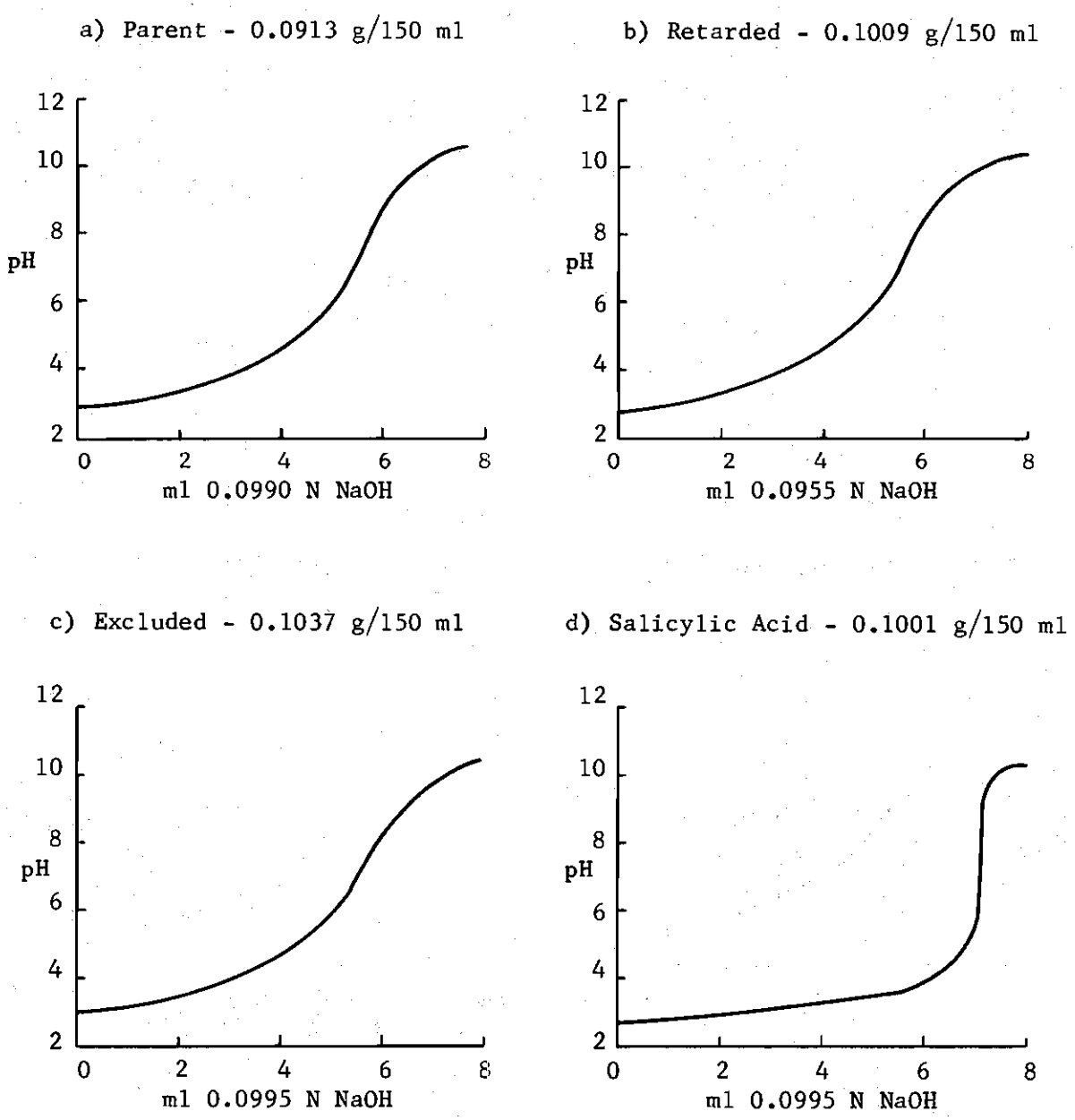


Figure 5. Simple Acid-Base Titration Curves (T = 25.00 ± .05°C, I = 0.1 with NaCl, 150 ml titrated)

The values of the inflection points were determined by a Grans plot and should correspond to the total carboxyl content of the organic. These values agree well with the general inflection point values inferred from the conductometric curves (Table 3), with the exception of the retarded total acidity. In this case the higher concentration of more acidic groups in the retarded fraction and the higher total concentration of acid in solution for the potentiometric titrations could suppress ionization at high pH values (as discussed in the section on theory, polyprotic acids), giving a somewhat flattened inflection point. The inflection point of the salicylic acid-NaOH curve agrees well with the theoretical.

The titration curve of the parent in 0.1 N $NaNO_3$ is given in Figure 6, and subsequent $pK(\bar{v})$ values are contained in Table 5, where α is the fraction dissociated carboxyl groups. A modified Henderson-Hasselbalch plot of the form

$$pK = pH - m \log \left(\frac{1-\alpha}{\alpha}\right)$$

is shown in Figure 7. The slope and intercept were obtained by a linear least-squares fit. The deviation of the slope from unity indicates the electrostatic interactions (Gregor et al., 1955), and the good linear fit up to pH 6.2 justifies the assumptions concerning the similarities of the acid strengths of the carboxyl groups.

Cd Acid-Base Titrations

The parent organic Cd acid-base titration pH and pCd curves and experimental conditions are contained in Figure 8, and values of log K_1 are in Table 6. These log K_1 values were obtained over the pH range from

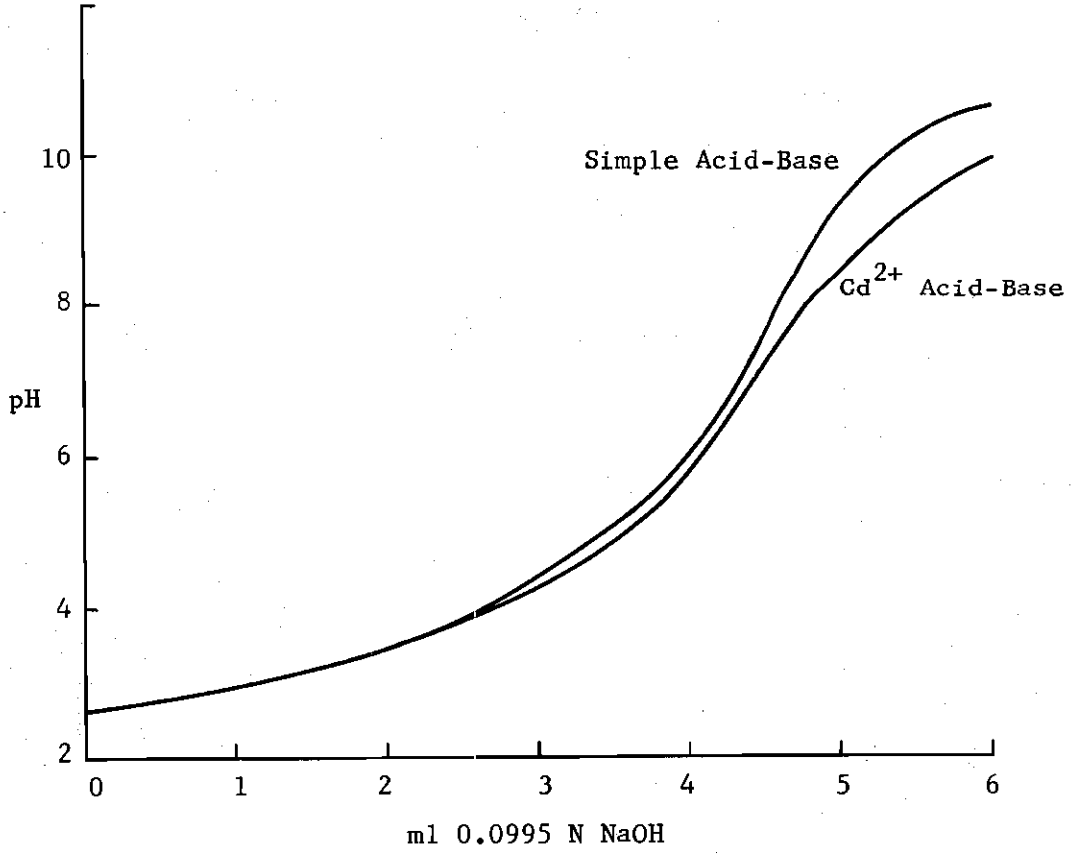


Figure 6. Parent Organic Simple Acid-Base Titration Curve and Cd Acid-Base Titration Curve (C_{Ao} = 0.1 g/100 ml, T = 25.00 ± .05°C, I = 0.1 ($NaNO_3$), 75 ml titrated. C_{Mo} = 0.977 x 10^{-4} m/ℓ in Cd acid-base titration.)

Table 5. $pK(\bar{v})$ Values for the Parent Organic Acid

$n = 6.00$ $\quad \alpha \equiv$ % dissociated (carboxyl groups) $= \frac{n-\bar{v}}{n}$

pH	$\bar{v}$	α	$pK(\bar{v})$
2.73	3.86	0.36	2.99
2.78	3.80	0.37	3.02
2.84	3.74	0.38	3.06
2.97	3.57	0.40	3.14
3.17	3.30	0.45	3.26
3.29	3.20	0.47	3.35
3.41	3.06	0.49	3.43
3.55	2.90	0.52	3.52
3.89	2.52	0.58	3.75
4.30	2.06	0.66	4.02
4.78	1.56	0.74	4.33
5.05	1.30	0.78	4.49
5.19	1.17	0.81	4.57
5.36	1.04	0.83	4.68
5.54	0.90	0.85	4.79
5.63	0.84	0.86	4.84
5.72	0.77	0.87	4.89
5.87	0.71	0.88	4.99
5.97	0.64	0.89	5.05
6.07	0.57	0.90	5.09
6.26	0.51	0.92	5.22
6.39	0.44	0.93	5.29
6.48	0.37	0.94	5.30
6.70	0.30	0.95	5.43
6.86	0.24	0.96	5.48
7.03	0.17	0.97	5.50

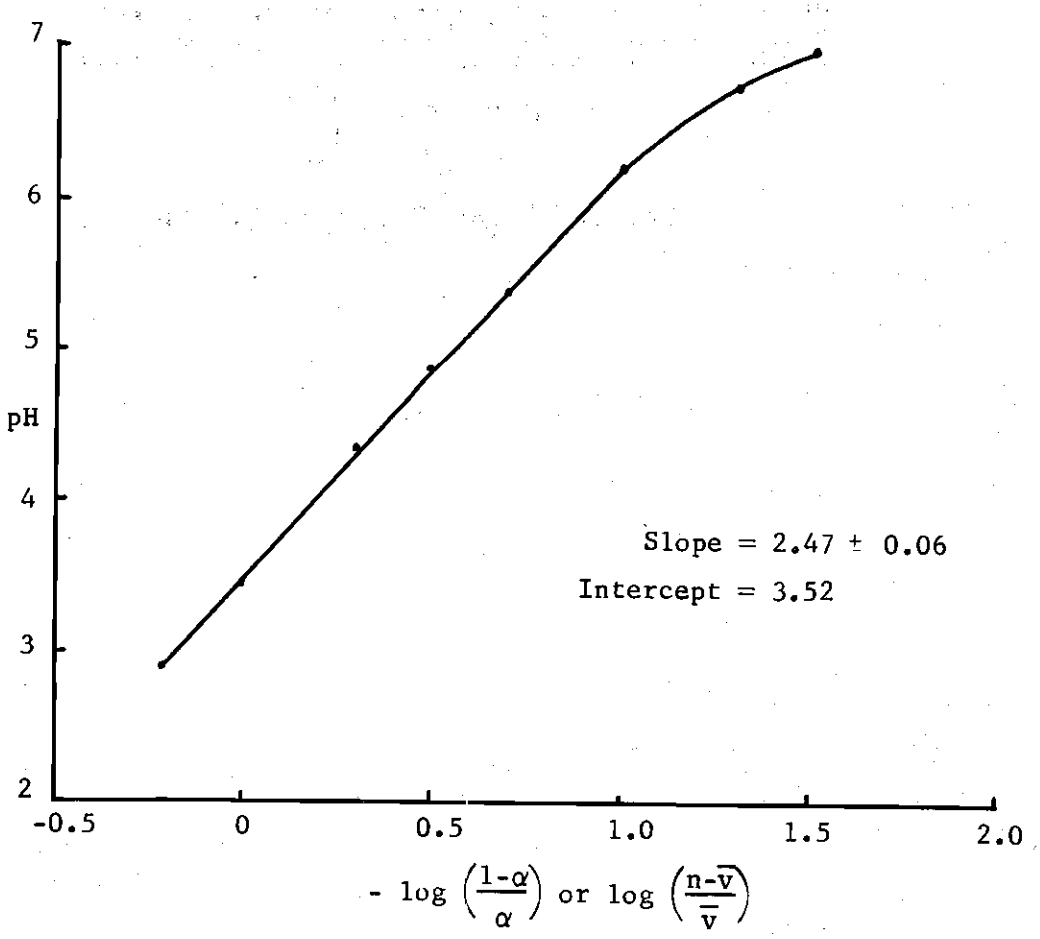


Figure 7. Henderson-Hasselbalch Plot for Parent Organic Simple Acid-Base Titration (Slope and intercept by a linear least squares fit)

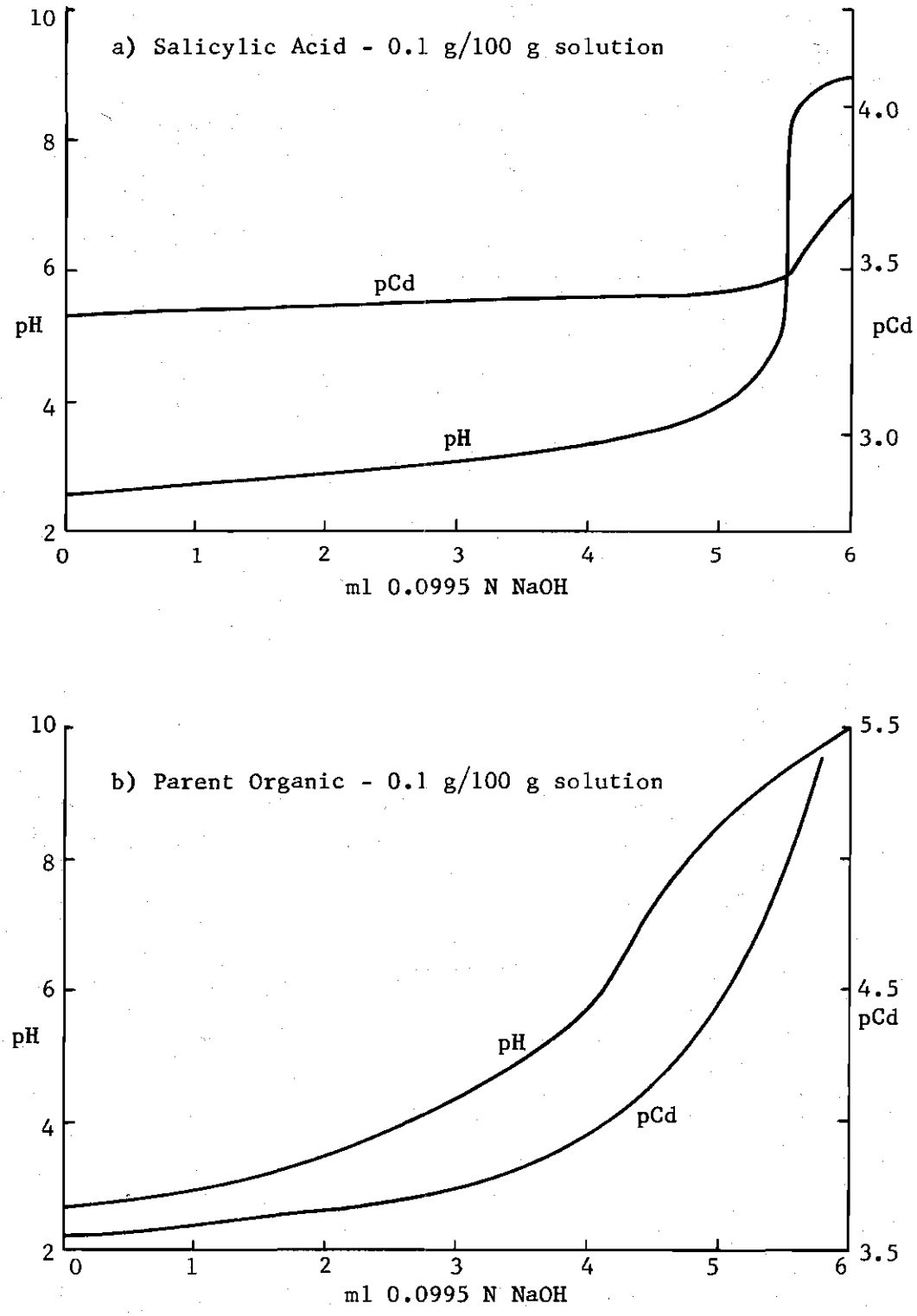


Figure 8. Cd Acid-Base Titration Curves (T = 25.00 ± .05°C, I = 0.1 with $NaNO_3$, $C_{M_O} = 0.0977 \times 10^{-3}$ M. pCd corresponds to $-\log[Cd^{2+}]$ measured by the Cd-electrode.)

Table 6. Log K_1 for the Parent Organic-Cd Complex from pH 4 to pH 6

pH	log K_1
4.12	2.50
4.32	2.51
4.53	2.54
4.76	2.57
5.03	2.61
5.10	2.63
5.17	2.64
5.25	2.65
5.33	2.67
5.50	2.70
5.61	2.71
5.71	2.73
5.83	2.73
6.10	2.76

4 to 6 because of the effects of hydrolysis of Cd at higher pH values (see the Appendix), and the response of the Cd electrode to H^+ at pH values less than 4 (present work). The log K_1 values are in good agreement with the log K values obtained by Schnitzer for divalent metals (Table 1) and are also seen to increase with increasing pH. The parent organic Cd acid-base pH titration curve is repeated in Figure 6 to show the effects of cadmium on the system as noted in the titration.

The salicylic acid Cd acid-base titration curves are also given in Figure 8. Due to the nature of the salicylic acid complex, the low pH, and the concentrations used, Cd^{2+} changes were just barely within the limits of the Cd electrode. These data are presented and discussed in Chapter V, and a typical standardization curve for the Cd electrode is shown in Figure 9.

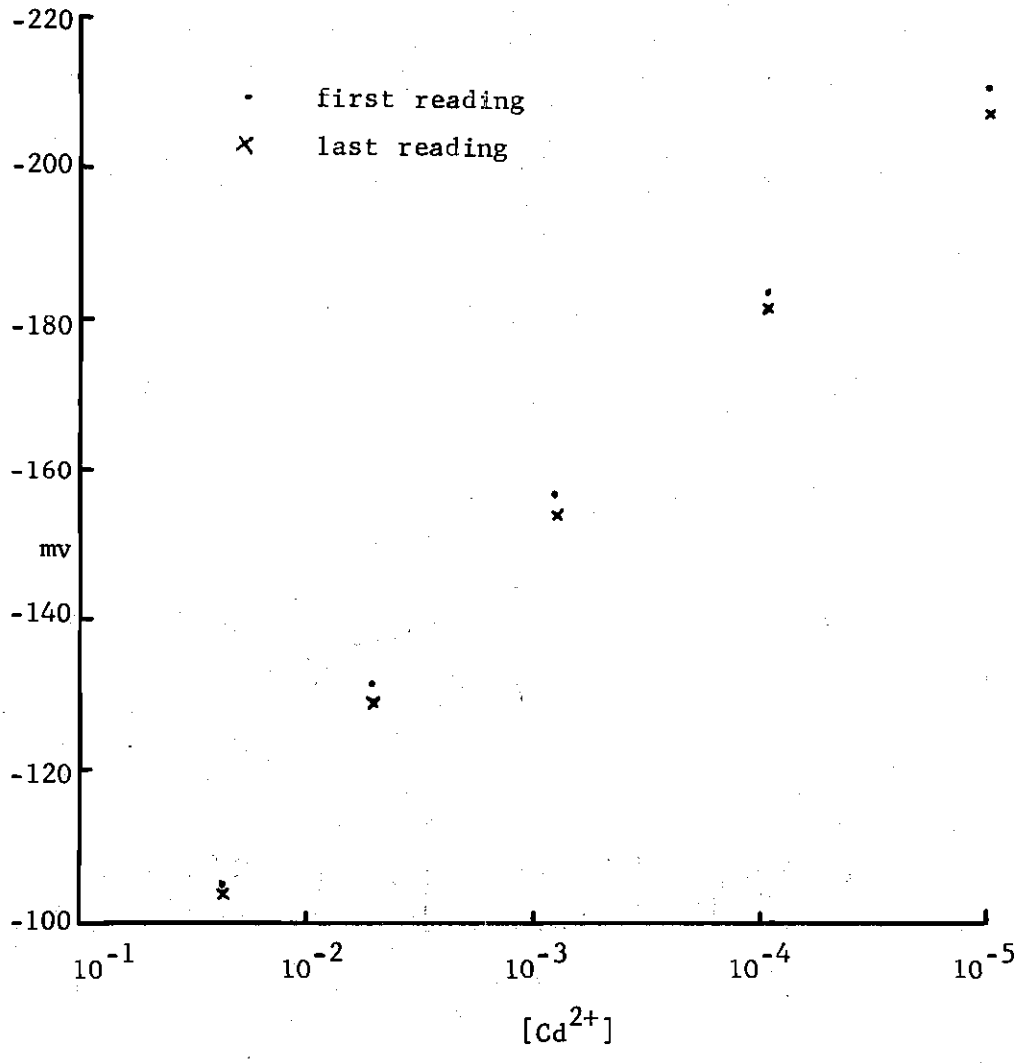


Figure 9. Typical Semi-Log Plot of $[Cd^{2+}]$ vs mv for Cd-Electrode, Showing Drift Over Approximately a Three Hour Period (30 mv slope - the low value for high (10^{-1} M Cd^{2+}) cadmium concentration was discarded)

CHAPTER V

DISCUSSIONS AND CONCLUSIONS

The results taken from the conductometric and acid-base potentiometric curves of the organic acid parent and fractions verify the previous assumption that this material is similar in composition to the fulvic acid examined by Martin (1973). The results of the salicylic acid titrations serve to indicate the validity of these techniques in determining concentrations of the carboxyls in river water organic fractions. As has also been noted, the modified Henderson-Hasselbach plot of the parent acid-base titration in $NaNO_3$ reveals a linear relationship, and thus the validity of the assumptions involved in obtaining these values.

The log K_1 values for Cd complexing (Table 6) are of the same magnitude as many of the values for other divalent metals (Table 1). Log K_1 is also observed to increase with increasing pH at constant ionic strength. While these values can be of great importance in assessing the magnitude of transport of various metals, the exact nature of the complexing process is still not well understood. In particular, the phenomenon of increasing log K values with increasing pH should be examined more carefully.

A detailed examination of the Cd-fulvic acid stability constant requires a closer look into the possible mechanisms of complexing. Following Gamble et al. (1970) and Cheam (1973), the complexing is assumed to be a salicylic type chelate (Figure 1a). As a rough approximation,

the dissociation constant of the phenolic hydroxyl of the salicylic group, pK_{d2}, is assumed to be roughly equivalent to that of the constant of the pure acid (pK_{d2} = 13.4 -- Chemical Rubber Company, 1972. See Table 7 for a comparison of pK values expected from data on small molecules in comparison to pK values calculated from the titration curve of a ribonuclease, where the number of sites on the molecule of carboxyl and phenolic hydroxyl groups is roughly comparable to fulvic acid - Tanford, 1961; p. 556).

Table 7. Intrinsic pK-Expected vs Obtained (Tanford, 1961, p. 556)

	$pK_{intrinsic}$ Expected from Data on Small Molecules	No. of Sites from Amino Acid Analysis	Data Obtained from Titration Curve	
			# Sites	pK_{int}
α-COOH	3.75	1	--	--
Side chain-COOH	4.6	10	10	4.7
Immadazole	7.0	4	4	6.5
α-NH_2	7.8	1		7.8
Phenolic	9.6	6	--	9.95
Side chain NH_2	10.2	10	10	10.2
Guanidyl	> 12	4	--	> 12

The carboxyl groups are adjacent to phenolic hydroxyls (Figure 1a), giving ligand sites identical to the type I group of Gamble et al. (1970). Thus, the complexing site takes on the form H_2L, where the singly dissociated species corresponds to HL^- (analogous to the singly ionized species of Figure 1a). Since the pK_{d2} value for the second dissociation is so far removed from the pH range of this work (pH 4-7), it will be assumed that

the $pK(\bar{v})$ values obtained previously are adequate in describing the carboxyl dissociation. This is seen to be true if Equation (24) is rewritten to include all possible forms:

$$C = (H_2L) + (HL^-) + (L^{2-}) + (CdL) \tag{26}$$

Equations (26) and (24) are analogous, where (H_2L) and (HL) from (26) and (24), respectively, denote the unionized species, (HL^-) and (L^-) denote the singly ionized carboxyl, and (L^{2-}) from (26) is the doubly dissociated salicylic group which is insignificant in the pH range of this experiment (see the Appendix).

The equation of chelation now becomes:

$$Cd^{2+} + HL^- = CdL + H^+ \tag{27}$$

where HL^- is used in the expression since its concentration can be determined. The corresponding equilibrium constant is:

$$\bar{K} = \frac{(CdL)[H^+]}{(Cd^{2+})(HL^-)} \tag{28}$$

Note that this corresponds to $K_1[H^+]$ (Equation 17), for now the singly ionized species is HL^- rather than L^-. The term $\bar{K}$ is taken from Gamble *et al.* (1970), and Table 8 contains the respective $\bar{K}$ values.

To compare this number with the theoretical $\bar{K}$ of salicylic acid, the following simple equilibrium reactions and equations are used:

Table 8. Values of H^+, $\bar{K}$, and Log K_c for the Cd Acid-Base Titrations

	pH	$[H^+] \times 10^5$	$\bar{K} \times 10^4$	log K_c [a]
	4.0	10.0	5.62	10.15
	4.13	7.41	4.54	10.05
	4.29	5.13	3.50	9.94
	4.41	3.89	2.86	9.36
Salicylic Acid	4.50	3.16	2.50	9.80
	4.56	2.75	2.39	9.78
	4.70	2.00	1.85	9.67
	4.91	1.22	1.21	9.48
	5.11	0.76	0.82	9.31
	5.80	0.16	0.18	8.65
		$[H^+] \times 10^6$	$\bar{K} \times 10^3$	
	4.12	75.9	23.8	11.77
	4.32	47.9	15.4	11.59
	4.53	29.5	10.2	11.41
	4.76	17.4	6.52	11.21
	5.03	9.33	3.83	10.98
Parent Organic	5.10	7.94	3.35	10.92
	5.17	6.76	2.91	10.86
	5.25	5.62	2.45	10.79
	5.33	4.68	2.11	10.72
	5.50	3.16	1.49	10.57
	5.61	2.45	1.22	10.49
	5.71	1.95	1.00	10.40
	5.83	1.48	0.79	10.30
	6.10	0.79	0.46	10.06
		$[H^+]$	$\bar{K}$	
Cu^{2+} Fulvic Acid [b]	3.0	1.0×10^{-3}	0.90	13.35
	5.0	1.0×10^{-5}	0.033	11.92

[a] Log K_c = 5.55 for Cd-Salicylic acid chelates (Perrin, 1964).

[b] From Gamble *et al.* (1970), as compared to their computed $\bar{K}$ figure of 0.003 for Cu^{2+}-salicylic-chelates.

$$H_2L = H^+ + HL^- \tag{29}$$

$$K_{d1} = \frac{[H^+](HL^-)}{(H_2L)} = K(\bar{v}) \tag{30}$$

representing the first dissociation of a salicylic group, and

$$HL^- = H^+ + L^{2-} \tag{31}$$

$$K_{d2} = \frac{[H^+](L^{2-})}{(HL^-)} \tag{32}$$

representing the second dissociation. From Equation (32)

$$(HL^-) = \frac{[H^+](L^{2-})}{K_{d2}} \tag{33}$$

and substituting (33) into (28)

$$\bar{K} = \frac{(CdL)K_{d2}}{(Cd^{2+})(L^{2-})} \tag{34}$$

or

$$\frac{\bar{K}}{K_{d2}} = \frac{(CdL)}{(Cd^{2+})(L^{2-})} = K_c \tag{35}$$

Log K_c, the chelation equilibrium constant of the completely dissociated salicylic acid group with cadmium, has been determined previously for pure salicylic acid (Perrin, 1964). Log K_c values calculated from Equation (35) for this experiment are also contained in Table 8. As is immediately obvious, the salicylic chelate type constant for the parent organic is

much larger than the value obtained previously for the pure system. In the same way, Gamble et al. (1970) noted that the $\bar{K}$ values for the Cu-chelates (Table 8) were also larger than the respective $\bar{K}$ which they calculated for the pure Cu-salicylic acid chelates, and that this discrepancy increased with decreasing pH. They explain the large values by noting that some of the dicarboxyl synthetic polymers also tend to have higher chelation values than the pure phthalic acid system but do not offer an explanation for the changing $\bar{K}$ with pH. A possible factor might be the importance of non-chelate complexes in the system, particularly for salicylic acid, where at low pH values the high pK_{d2} severely limits the amount of L^{2-} available as a ligand for the copper chelate. Thus, at low pH levels the amount of metal which is non-chelate complexed is important in relation to the amount chelated, and it can effectively increase any general equilibrium constant which cannot distinguish between the two types of complexes. The change in $\bar{K}$ with pH could be the result of the interplay between the two constants, a non-chelate (Figure 1c) value and a salicylic chelate (Figure 1a) value.

At this time it is important to note that an inherent assumption in assigning a phenolic hydroxyl group to all carboxyls is that the system is entirely composed of salicylic type functional groups. To circumvent this problem, the exact nature of the organic must be understood. But since a second inflection point corresponding to the more acidic carboxyls was absent in the parent simple acid-base titration curve, a value cannot be given for these groups with any degree of certainty. Table 9 contains the values of log K_1 computed using the minimum of the parent

conductometric as an estimate of salicylic groups, and in the pH range from 5-6 it was assumed that complete dissociation had occurred with the carboxyl groups. It can be seen that the log K_1 values obtained using these assumptions do not radically differ from the values computed using $K(\bar{v})$ and total carboxyl concentrations. The total carboxyl concentration values will be used since any carboxyl could be important in non-chelate type complexes.

Table 9. Log K_1 Values Using the Conductometric Minimum as an Estimate of Complexing Sites

pH	Log K_1	Log K_1[a]
4.12	2.49	2.50
4.32	2.53	2.51
4.53	2.58	2.54
4.76	2.64	2.57
5.03	2.71	2.61
5.10	2.73	2.63
5.17	2.75	2.64
5.25	2.76	2.65
5.33	2.78	2.67
5.50	2.81	2.70
5.61	2.84	2.71
5.71	2.86	2.73
5.83	2.88	2.73
6.10	2.93	2.76

[a]Log K_1 values obtained using total carboxyl concentration and $pK(\bar{v})$ values (Table 6).

In order to describe the phenomenon of non-chelate complexation, an additional equilibrium reaction must be examined:

$$Cd^{2+} + HL^{-} = CdHL^{+} \tag{36}$$

analogous to Figure 1c. The corresponding equilibrium constant is:

$$K_a = \frac{(CdHL^{+})}{(Cd^{2+})(HL^{-})} \tag{37}$$

In Equation (28), the (CdL) term used to determine $\bar{K}$ was determined from (23) and is actually a value for all cadmium complexed, or Cd_c. Thus, Equation (28) is rewritten

$$\bar{K} = \frac{Cd_c[H^{+}]}{(Cd^{2+})(HL^{-})} \tag{38}$$

but, since non-chelate and chelate complexes are present,

$$Cd_c = (CdHL^{+}) + (CdL) \tag{39}$$

and substituting into (38),

$$\bar{K} = \frac{((CdHL^{+}) + (CdL))[H^{+}]}{(Cd^{2+})(HL^{-})} \tag{40}$$

The salicylic type chelate will be rewritten as

$$Cd^{2+} + HL^{-} = CdL + H^{+} \tag{41}$$

$$K_b = \frac{(CdL)[H^{+}]}{(Cd^{2+})(HL^{-})} \tag{42}$$

The values K_a and K_b describe non-chelation and chelation equilibria, respectively, and have distinctly different meanings. Note that both still describe a 1:1 complex between carboxyl site and complexed metal. By substituting Equations (37) and (42) into (40), the final form is obtained:

$$\bar{K} = K_a[H^+] + K_b \tag{43}$$

Thus, K_a and K_b values can be obtained from the slope and intercept, respectively, of a plot of $[H^+]$ vs $\bar{K}$.

Figure 8 contains the salicylic acid Cd acid-base titration curve, and Figure 10 is a plot of the $[H^+]$ vs $\bar{K}$ values given in Table 8. K_a and K_b were determined by a linear least squares fit and are contained in Table 10.

Table 10. Log K_a, K_b, and Log K_c for Organic Acids

Metal	Acid	Log K_a	K_b	Log K_c[a]
Cd^{2+}	Salicylic	0.56	4.2×10^{-6}	8.0[b]
	Parent Organic	2.59	4.3×10^{-4}	9.7
Cu^{2+}	Fulvic	2.94	0.024	11.8[c]

[a] $\text{Log } K_c = \log \frac{K_b}{K_{d2}}$

[b] Log K_c for Cd^{2+}-salicylic acid = 5.55 (Perrin, 1964).

[c] Log K_c for Cu^{2+}-salicylic acid = 10.64 (Perrin, 1964).

The log K_c value which is also included is determined from Equation (35) with K_b, the correct chelating constant, being used instead of $\bar{K}$. This

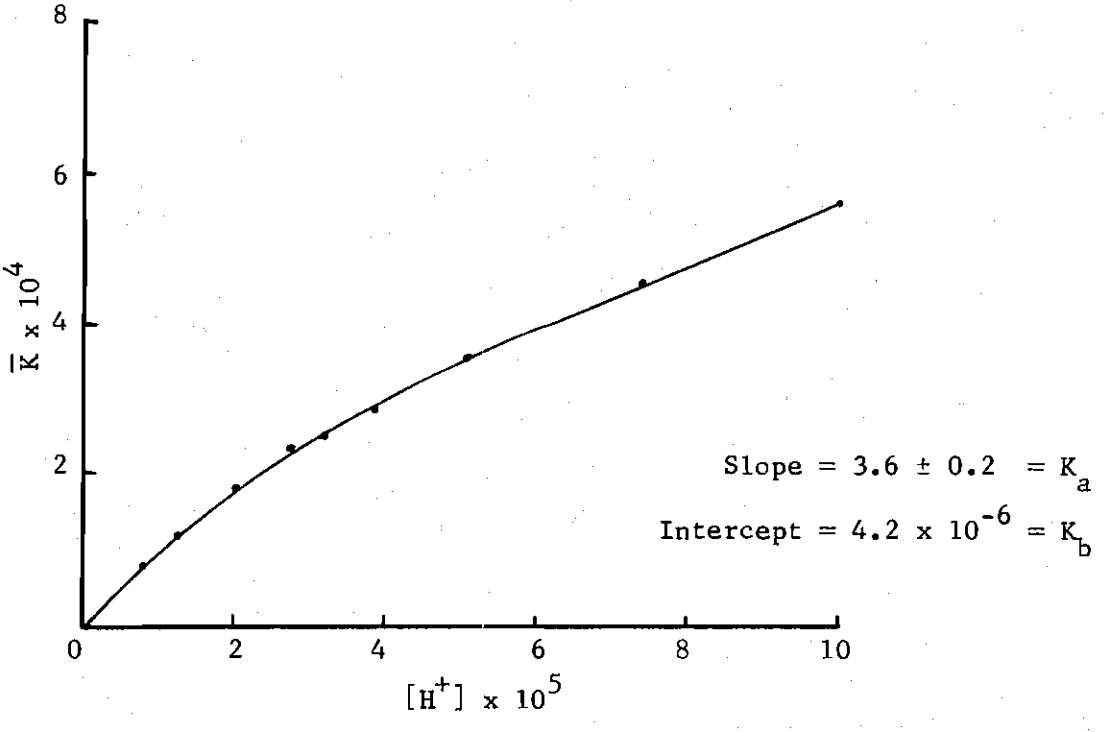


Figure 10. $[H^+]$ vs $\bar{K}$ for Salicylic Acid (Slope and intercept by linear least squares over entire region. Initial slope ≈ 10 giving log K_a closer to previously obtained values.)

value is much higher than that obtained by Perrin. An examination of Figure 10 shows the obvious deviation of the slope from a constant, with the slope, K_a, approaching 10 at low $[H^+]$. The apparent explanation is the small amount of complexing occurring in the low pH range which puts the amount of complexed cadmium at the very limits of the Cd-electrode. As the pH increases more cadmium is chelated, and the response improves. The linear least squares fit of the line gave a K_a value of 3.6, or log K_a of 0.56. It is interesting to note that this is comparable to the values given in Sillen et al. (1971, p. 483) obtained by two experimenters performing polarographic experiments in 1 N $NaNO_3$ and 1 N KNO_3, and whose log K_a values were 0.96 and 0.60, respectively. While the difference in ionic strength prevents a direct comparison and indicates that this log K_a value (0.56) is too low, the slope of Figure 10 can be seen to approach these values. This is a good indication of the validity of this technique.

A plot of $[H^+]$ vs $\bar{K}$ for the parent organic Cd acid-base titration is contained in Figure 11 using the values in Table 8. K_a and K_b were obtained with greater precision by a linear least squares fit because of the obvious linearity of the plot and the large deviation of the intercept from zero. K_a and K_b values are contained in Table 10. The K_a value is interesting in that it indicates the effects of non-chelate complexes at low pH levels. By a simple manipulation of Equations (37) and (42), the following relationship is obtained:

$$\frac{(CdHL^-)}{(CdL)} = \frac{K_a}{K_b}[H^+] \qquad (44)$$

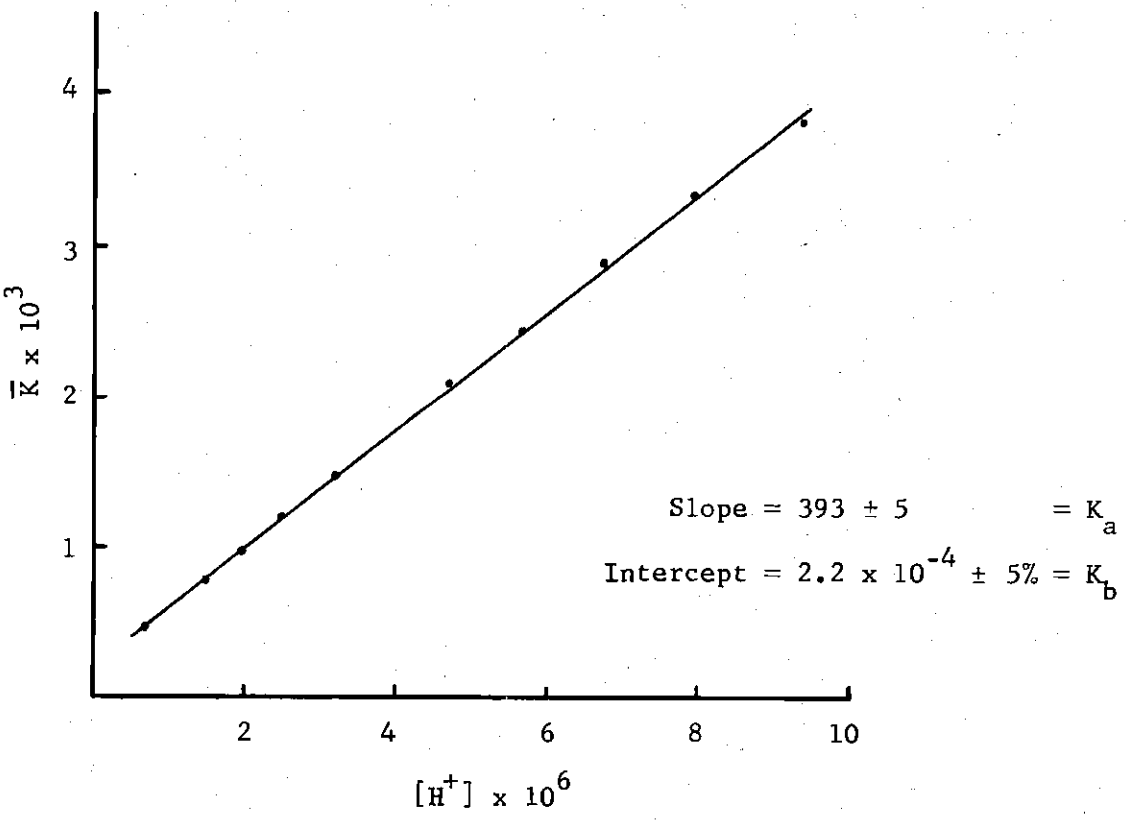


Figure 11. $[H^+]$ vs $\bar{K}$ for the Parent Organic (slope and intercept by linear least squares)

Thus, at a pH of 6.3 both species will be equally present, with the chelate predominating at a higher pH, and the non-chelate complex predominating at lower pH levels. The overall complexing constant of the system which does not differentiate between the two will be a function of pH. Note that Figure 6 shows little H^+ displacement with cadmium in the system, indicating that Cd-river water organic chelates are not important at low pH.

The value of log K_c obtained here from K_b is also in Table 10 and is much higher than the figure by Perrin. The reason for this discrepancy in log K_c is unclear at this point. A possible explanation might be the incorrect assumption of a pK_{d2} value, or the complex might actually tend to be much stronger in this system, as Gamble et al. (1970) assumed for their Cu-fulvic acid complex. Other log K_c values determined by other methods for cadmium complexing could not be found for verification.

The $\bar{K}$ values at pH 3 and 5 from the paper by Gamble et al. (1970) were plotted to obtain a rough approximation of K_a and K_b. These values are also given in Table 10 and indicate that the K_c value for Cu-fulvic acid is still slightly higher than the literature value, and non-chelate complexes are also important at low pH levels. Because of the stronger chelate formed in this system, the pH of a 1:1 ratio between non-chelated complex and chelate is 4.6.

Results for Cu(II)-fulvic acid chelation by Cheam (1973, Figure 1) are reproduced in Figure 12 and indicate that, for a particular pH, $\bar{K}$ decreases with increasing apparent acid concentration (mole fraction), as well as showing how $\bar{K}$ increases with $[H^+]$ at constant concentrations.

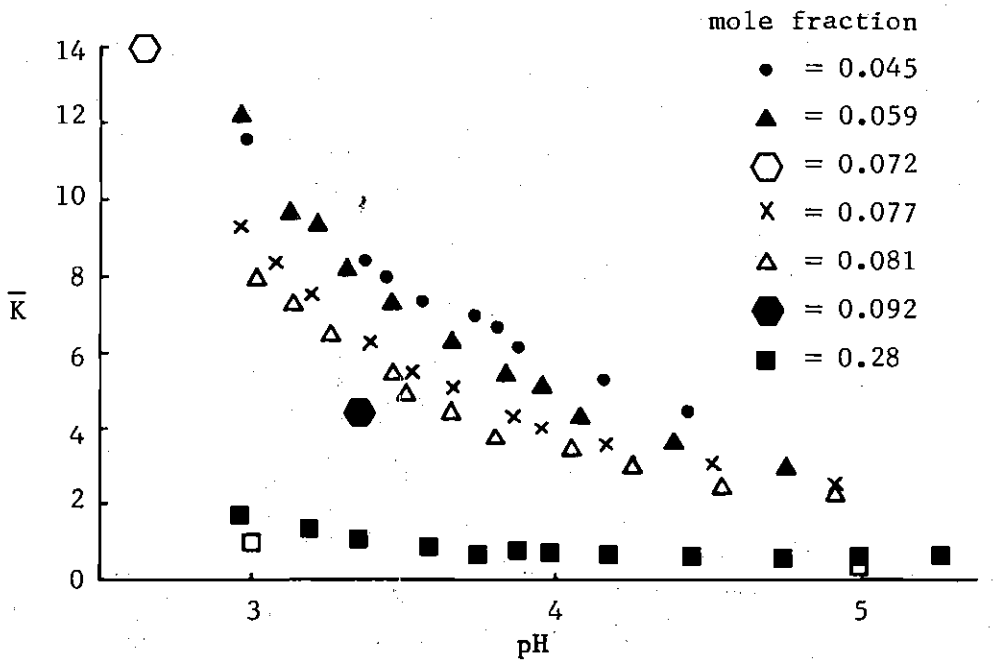


Figure 12. pH vs $\bar{K}$ for Cu(II)-Fulvic Acid (Data from Cheam (1973, Fig. 1). There is decreasing slope with increasing concentration (mole fraction).)

It is interesting to note, however, that the $\bar{K}$ values appear to converge at a single point in the high pH region. Apparently, the major factor affecting the system is the changing non-chelate complex K_a values at different organic acid concentrations. This also appears to be related to the ionic interactions arising due to the polyprotic nature of the organic and the proximity of the charged non-chelate complexes to one another. High concentrations would thus be less conducive to this non-chelate complexation phenomenon.

These results indicate that the phenomena of non-chelation equilibria are important and should not be overlooked, particularly for the metals which do not tend to form strong chelates. The implications are that in waters of low pH (3 to 5) much of the metal may be merely non-chelate complexed and more easily removed. The metal associated with organics in waters with higher pH levels will subsequently be more firmly bound to the organic molecule and will have less of a tendency of being displaced. These results also seem to indicate one possible reason for the large change in log K stability values with pH in constant ionic strength media.

CHAPTER VI

RECOMMENDATIONS

Much more work can be accomplished in determining the nature of these complexes. Experiments should be conducted at different ionic strengths for extrapolation of thermodynamic stability constants. A more detailed study of the Cd-salicylic acid system and other Cd-organic acid systems, such as phthalic acid, should also be conducted, realizing the limitations imposed by the low solubilities of many of these compounds.

The use of selective ion electrodes as a method for following complexing is a relatively new and powerful technique which has already been used by a few experimenters in the field of fulvic acid complexing (Cheam, 1973, and Manning et al., 1973). More work must be done in assessing carefully the response of these electrodes as a function of time, temperature, and pH, so that a more accurate appraisal can be made concerning their effectiveness. The work conducted in this laboratory is perhaps as qualitatively useful as it is quantitative, but the attainment of numbers to a greater degree of precision and accuracy will require much more work and the eventual improvement of the selective ion electrodes.

APPENDIX

$CdNO_3^+$ Complexes

According to the specifications in the Orion Cadmium Electrode Instruction Manual, NO_3^- will have an insignificant effect on the free Cd^{2+} in solution. The standardization plot (Figure 9) demonstrated a linear response with activity over most of the concentration range, with the deviation at high concentration being opposite to that expected if $CdNO_3^+$ complexing were to appreciably occur. Values for log K_1 (compiled by Sillen et al. (1964, 1971), where

$$K_1 = \frac{(CdNO_3^+)}{(Cd^{2+})(NO_3^-)}$$

were diverse and ranged from no evidence of complexing to a log K of 0.40 at zero corrected ionic strength. More recent work indicated a log K of - 0.42, obtained from experiments at 44°C and variable ionic strengths. Due to the absence of values at the experimental conditions used here and the diversity of numbers, this figure will be used to give a rough estimate of possible complexing. The ratio of complexed to uncomplexed Cd is simply

$$\frac{(CdNO_3^+)}{(Cd^{2+})} = K_1(NO_3^-) \qquad (45)$$

If log K_1 = - 0.42, and $(NO_3^-) \simeq 0.1$ N, then

$$\frac{(CdNO_3^+)}{(Cd^{2+})} = 0.038, \text{ or } 3.8\%$$

The value of this figure is in doubt, and near the response limit of the electrode. Changes in log K_1 would be insignificant since the (Cd) and (L) in Equation (17) would remain constant (the concentration of Cd^{2+} is determined directly, and the small change in (CdL) in Equation (25) is small compared to C_A), and a change in (CdL) of 4% would alter log K_1 by + 0.02. $CdNO_3^+$ complexing was thus ignored.

$CdCl^+$ Complexes

$CdCl^+$ complexing is quite extensive, with log K_1 in the range of 1 to 2. The equation expressing the ratio of $CdCl^+$ to Cd^{2+} is analogous to Equation (45):

$$\frac{(CdCL^+)}{(Cd^{2+})} = K_1(Cl^-) \qquad (46)$$

If (Cl^-) were 10^{-1} M, and log K taken to be 1.5, then

$$\frac{(CdCl^+)}{(Cd^{2+})} = 0.32, \text{ or } 32\%$$

An error of this magnitude would change log K_1 by + 0.1; therefore, $NaNO_3$ was used as an ionic strength adjustor.

$CdOH^+$ Complexes

Again according to the specifications in the Orion Cd-Electrode

Reference Manual, $CdOH^+$ formation would be insignificant at the Cd concentration and pH of this experiment. $Log\ ^*K_1$, where

$$^*K_1 = \frac{[CdOH^+][H^+]}{[Cd^{2+}][H_2O]} \tag{47}$$

is given a value of - 7.92 at zero corrected ionic strength and 25°C (compiled by Sillen et al., 1971), which would correspond to

$$\frac{[CdOH^+]}{[Cd^{2+}]} = \frac{^*K_1}{[H^+]} \tag{48}$$

where $[H_2O] = 1$ is assumed. At pH 6.1, the upper pH range used to calculate Cd-complexing,

$$\frac{[CdOH^+]}{[Cd^{2+}]} = 0.01, \text{ or } 1\%$$

Other $log\ ^*K$ values in the compilations indicate even less complexing, and so $CdOH^+$ complexes were ignored.

L^{2-} Concentrations

In the pH range from 4 to 6 it was assumed that (L^{2-}) was insignificant, i.e. the doubly dissociated salicylic group was not present in experimentally determinable quantitites. This is easily verified by rearranging Equation (33) to

$$\frac{(L^{2-})}{(HL^-)} = \frac{K_{d2}}{[H^+]} \tag{49}$$

If $pK_{d2} = 13.4$, then at pH 6.1

$$\frac{(L^{2-})}{(HL^{-})} = \frac{10^{-13.4}}{10^{-6.1}} = 10^{-7.3}$$

The concentration of (L^{2-}) would be extremely small, and is ignored.

Calculation 1. Determination of $pK(\bar{v})$ for the Parent Organic Acid

The $pK(\bar{v})$ value expresses the general overall dissociation constant of a large polyprotic acid at a particular pH, and is calculated from Equation (15), using $\bar{v}$ and n. $\bar{v}$ is determined from Equation (8)

$$\bar{v} = n - \frac{(H^+) - \frac{K_w'}{(H^+)} + C_B}{C_A} \tag{8}$$

n = 6.00 meq/g, determined directly from the inflection point of the parent organic acid titration curve (Figure 6). K_w' is assumed to be 10^{-14}. At pH 4.3 $[H^+]$ is less than 1% as large as C_B, and decreases rapidly, and so is used rather than (H^+). C_A is simply calculated

$$C_A = \frac{V}{V+v} C_{Ao} \tag{50}$$

where v is the amount of titrant added, V the original solution volume (75.00 ml), and C_{Ao} the original acid concentration (1 g/ℓ).
Similarly,

$$C_B = \frac{v}{V+v} C_{Bo} \tag{51}$$

where C_{Bo} is the concentration of the titrant (0.1005 m). $pK(\bar{v})$ is then

calculated from Equation (15)

$$pK(\bar{v}) = pH - \log\left(\frac{n-\bar{v}}{\bar{v}}\right) \tag{15}$$

For example, at pH 5.05, v is 3.500, and

$$C_A = \left(\frac{75.00}{75+3.5}\right) 1 = 0.955$$

$$C_B = \left(\frac{3.50}{75.00+3.50}\right) 0.1005 = 4.4 \times 10^{-3}$$

$$\bar{v} = 6.00 \times 10^{-3} - \frac{8.91 \times 10^{-6} - \frac{10^{-14}}{8.91 \times 10^{-6}} + 4.4 \times 10^{-3}}{9.55 \times 10^{-1}} = 1.38 \times 10^{-3}$$

$$pK(\bar{v}) = 5.05 - \log \frac{6.00 \times 10^{-3} - 1.38 \times 10^{-3}}{1.38 \times 10^{-3}} = 4.49$$

Table 11 contains pH and v data for the parent organic simple acid-base titration.

Calculation 2. Determination of Cd-Parent Organic Stability Constants

The log K_1 values were determined from the Cd acid-base titrations, and the experimental mv, pH, and v data for the parent organic and salicylic acid titrations are given in Table 12. K_1 has been previously defined as

$$K_1 = \frac{(CdL)}{(Cd^{2+})(L^{2-})} \tag{25}$$

(Cd^{2+}) is determined from the relation

Table 11. Simple Acid-Base Titration Data for the Parent Organic Acid

pH	v
2.73	0.200
2.78	0.400
2.84	0.600
2.97	1.000
3.17	1.500
3.29	1.700
3.41	1.900
3.55	2.100
3.89	2.500
4.30	2.900
4.78	3.300
5.05	3.500
5.19	3.600
5.36	3.700
5.54	3.800
5.63	3.850
5.72	3.900
5.87	3.950
5.97	4.000
6.07	4.050
6.26	4.100
6.39	4.150
6.48	4.200
6.70	4.250
6.86	4.300

Table 12. Cd Acid-Base Titration Data for the Parent Organic and Salicylic Acids

Parent Organic Acid			Salicylic Acid		
v	pH	mv	v	pH	mv[a]
0	2.68	- 166.0	0	2.59	- 162.1
0.300	2.75	- 166.2	0.200	2.63	- 162.2
0.600	2.84	- 166.5	0.604	2.67	- 162.3
1.000	2.97	- 167.0	1.104	2.74	- 162.3
1.300	3.09	- 167.3	1.300	2.77	- 162.2
1.700	3.28	- 167.9	1.603	2.82	- 162.4
2.000	3.97	- 168.3	2.001	2.89	- 162.9
2.200	3.61	- 168.8	2.300	2.95	- 163.2
2.403	3.76	- 169.2	2.600	3.02	- 163.2
2.600	3.94	- 169.8	3.102	3.13	- 163.5
2.803	4.12	- 170.4	3.400	3.20	- 163.5
3.000	4.32	- 171.2	3.700	3.29	- 163.6
3.200	4.53	- 172.0	4.000	3.38	- 163.6
3.400	4.76	- 173.0	4.300	3.49	- 163.7
3.600	5.03	- 174.0	4.600	3.63	- 163.8
3.650	5.10	- 174.4	4.802	3.76	- 164.0
3.700	5.17	- 174.7	5.000	3.81	- 164.0
3.750	5.25	- 175.1	5.098	4.00	- 164.1
3.800	5.33	- 175.4	5.200	4.13	- 164.2
3.900	5.50	- 176.1	5.300	4.29	- 164.2
3.952	5.61	- 176.5	5.350	4.41	- 164.2
4.002	5.71	- 176.7	5.380	4.50	- 164.2
4.050	5.83	- 177.8	5.400	4.56	- 164.2
4.150	6.10	- 178.8	5.430	4.70	- 164.3
4.200	6.26	- 178.8	5.467	4.91	- 164.3
4.250	6.42	- 179.4	5.490	5.11	- 164.4
4.302	6.58	- 180.0	5.520	5.80	- 164.8
4.352	6.76	- 180.6	5.550	7.91	- 167.0
4.400	6.92	- 181.2	5.582	8.48	- 167.3
4.450	7.11	- 181.9	5.600	8.64	- 167.7

[a] mv values are corrected for drift.

$$(Cd^{2+}) = \frac{[Cd^{2+}]}{\gamma^{+}_{Cd^{2+}}}$$

where $[Cd^{2+}]$ is the activity of free cadmium determined directly from mv (see Figure 9), and $\gamma^{+}_{Cd^{2+}}$ is given the value 0.41 from the Fisher Cd-Electrode manual. (CdL) is determined from the relationship

$$C_M = (Cd^{2+}) + (CdL) + (CdX) \qquad (23)$$

(CdX), the concentration of NO_3^{2-} and OH^- complexes with Cd^{2+}, is assumed to be zero as outlined previously, and

$$C_M = \frac{V}{V+v} C_{Mo} \qquad (52)$$

C_{Mo} is the original total cadmium concentration (0.977×10^{-4} m) and V is the original solution volume (75.00 ml). (L) is defined as

$$(L) = \frac{K(\bar{v})\ (C_A - (CdL))}{K(\bar{v}) + [H^+]} \qquad (25)$$

$K(\bar{v})$ for different pH values is obtained from Table 5 by interpolation, and C_A is calculated from Equation (50) which is identical for these titrations.

Thus, at pH 5.71, the value of v is 4.00 ml and the value of mv is - 176.9, and

$$(Cd^{2+}) = \frac{1.17 \times 10^{-4}}{0.41} = 2.86 \times 10^{-4}$$

$$C_M = \left(\frac{75}{75+4}\right) 9.77 \times 10^{-4} = 9.28 \times 10^{-4}$$

$$(CdL) = 9.28 \times 10^{-4} - 2.86 \times 10^{-4} = 6.42 \times 10^{-4}$$

$$(L) = \frac{1.29 \times 10^{-5} \ (5.70 \times 10^{-3} - 6.42 \times 10^{-4})}{1.29 \times 10^{-5} + 1.95 \times 10^{-6}} = 4.4 \times 10^{-3}$$

$$K_1 = \frac{(6.42 \times 10^{-4})}{(2.86 \times 10^{-4})(4.4 \times 10^{-3})} =$$

$$\log K_1 = 2.73$$

$\overline{K}$ has been defined as

$$\overline{K} = K_1 \cdot [H^+]$$

and K_c as

$$K_c = \frac{\overline{K}}{K_{d2}}$$

or

$$K_c = \frac{K_b}{K_{d2}}$$

The solution of these is straightforward ($pK_{d2} = 13.4$), as is the determination of K_a and K_b (Equation (43); Figures 10 and 11).

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